# THE REACTIONS OF *p*-QUINONEDIBENZIMIDES AND RELATED COMPOUNDS

BY

DONALD STANLEY ACKER

B.S., Allegheny College, 1949

## AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1952

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R. UNIV. BIBLIOTHEEK LEIDEN

# THE REACTIONS OF *p*-QUINONEDIBENZIMIDES AND RELATED COMPOUNDS

## Introduction

Recent investigations (1) have revealed that various N-substituted quinone imines are stable chemical compounds and will enter into many of the reactions characteristic of quinones. Most of this research has been carried out using the benzenesulfonyl group to stabilize the quinoid system. More recently, it has been shown that various acyl and aroyl derivatives of *p*-phenylenediamine can be oxidized to give stable quinone diimides.

The purpose of this investigation was to study the reactions of *p*-quinonedibenzimide and related compounds. It was of interest to attempt syntheses with these compounds which failed or gave undesired products with the *p*-quinonedibenzenesulfonimides.

## Discussion Of Results

2-Chloro-*p*-quinonedibenzimide reacted with hydrogen chloride to give exclusively 2,6-dichloro-*p*-phenylenedibenzamide. This structure was proved by unequivocal synthesis. Oxidation to the corresponding diimide and treatment with hydrogen chloride gave a mixture from which only a small amount of the expected trichloro diamide could be isolated. 2,3,5,6-Tetrachloro-*p*-phenylenedibenzamide was synthesized from 1,2,4,5-tetrachlorobenzene. This product was oxidized to the corresponding diimide.

*p*-Quinonedicarbobenzoxyimide was prepared by oxidation of *p*-phenylenedibenzylcarbamate. Addition of hydrogen chloride, oxidation of this product and subsequent treatment with hydrogen chloride led to a mixture of dichloro diamide isomers. Oxidation of this mixture and treatment with hydrogen chloride gave a good yield of 2,3,5-trichloro-*p*-phenylenedibenzyl-

carbamate. This compound was easily converted to 2,3,5-trichloro-*p*-phenylenediamine either by hydrolysis or hydrogenolysis. 2-Chloro-*p*-quinonedicarbethoxyimide was prepared and reacted with hydrogen chloride to give a mixture of isomeric dichloro-*p*-phenylenediethylcarbamates from which two were isolated in a pure state.

*p*-Quinonedibenzimide, *p*-quinonedicarbethoxyimide, and *p*-quinonedicarbobenzoxyimide reacted with organic acids to form esters which can be hydrolyzed to the corresponding 2-hydroxy diamides. This reaction has not been observed with quinones or in previous work on *p*-quinonedibenzenesulfonimides. The scope of the reaction was investigated and it was found to be quite general. A wide range of acids was reacted to give stable adducts. The presence of a chloro or methyl group in the ring did not inhibit the reaction. A procedure was developed whereby organic acids could be added to *p*-quinonedibenzenesulfonimide. In the presence of a catalyst such as boron fluoride, the 2-acyloxy-*p*-phenylenedibenzenesulfonamides were formed.

It was found that various other reagents could be readily reacted with *p*-quinonedibenzimide to form monosubstituted dibenzamides. Addition of thiophenol gave 2-phenylmercapto-*p*-phenylenedibenzamide which could be oxidized to the corresponding diimide. Addition of a second mole of thiophenol gave the diphenylmercapto adduct. Methanol and ethanol were added in the presence of a boron fluoride catalyst. The presence of the methoxy group in the 2-position was demonstrated by unequivocal synthesis. Active methylene compounds such as acetylacetone and diethylmalonate were added in the presence of sodium methoxide to give the corresponding monoadducts.

Morpholine, piperidine and aniline were added to *p*-quinonedibenzimide to give the corresponding monosubstituted dibenzamides. The easy isolation of a monoadduct is in direct contrast to previous results with *p*-quinonedibenzenesulfonimide, where the same reactions led to many products of

1,2- and 1,4-addition and reoxidation (2).

*p*-Quinonedibenzimide did not react readily with conjugated dienes. Cyclopentadiene, one of the more reactive dienes, gave only a monoadduct. Phenol was the only compound which reacted with the diimide under Friedel-Crafts conditions.

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## VITA

The author was born on November 14, 1925 near Saegerstown, Pennsylvania. He graduated from Saegerstown High School in June, 1942. After serving with the United States Army Air Forces, he entered Allegheny College in September, 1946, where he received the degree of Bachelor of Science in Chemistry, with honors, in June, 1949. In September of that year he entered the Graduate College of the University of Illinois. He held a Teaching Assistantship for the academic year 1949-50, the Standard Oil Company (Indiana) Fellowship during 1950-51 and the Allied Chemical and Dye Corporation Fellowship during 1951-52.